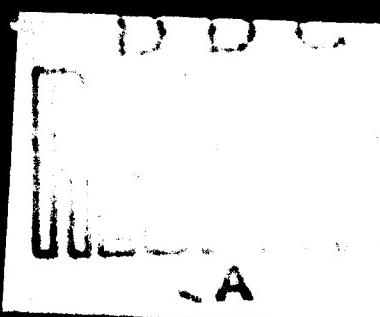


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PROPULSION TECHNOLOGY AND PROJECT ENGINEERING DEPARTMENT
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INVESTIGATION OF LUBRICANT CONCEPTS APPLICABLE
TO FUTURE NAVY AIRCRAFT PROPULSION SYSTEMS

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INTRODUCTION

A lubricant must possess many specific properties and performance characteristics to meet the requirements of a particular application. The reduction of friction and wear and the removal of heat are generally accepted as the major functions of a lubricant. While providing these functions the lubricant composition must be such that it is compatible with all other materials throughout the system. Fluid properties must not compromise equipment operation throughout the entire operating environment. Many other properties, such as volatility, foaming, and corrosiveness must be controlled. In a gas turbine engine, lubricants are subjected to severe thermal environments. They must lubricate high temperature bearings and gears and provide the medium by which heat is removed from these components. As engine technology advances, as aircraft capable of operating at higher speeds are developed, and as the trend toward lighter more powerful aircraft engines increases, the energy density of the equipment and higher temperatures become an inherent characteristic of the lubrication system. The assessment of the lubrication needs with respect to this thermal environment in gas turbine propulsion systems is the subject of this report.

The work reported herein completes the requirements of reference 1.

CONCLUSIONS

1. General. A study concerning the lubrication needs of future Navy aircraft systems showed that the ester-based fluids have the potential to satisfy the anticipated requirements. However, some work is needed to increase the thermal oxidative stability of ester lubricants. An extension of thermal capabilities of this type of lubricant can have significant pay-offs in reliability and weight savings of future propulsion systems.
2. Research efforts dealing with "new" base materials cannot be supported by any identifiable future propulsion system. However, studies of the effects of lubricant properties on engine design and performance show that for "high Mach" applications severe weight penalties arise when design is constrained by lubricant thermal capabilities.
3. Inerted Ester Systems. Inerting of systems using ester-based lubricants can raise the functional capability of this type of lubricant from 204°C (400°F) to possibly 316°C (600°F). However, to reach this potential it is essential to exclude virtually all oxygen from the system and to condense and return volatile components of the lubricants to the bulk oil.
4. Polyphenyl Ether. Considerable improvement in performance of a polyphenyl ether basestock can be derived from use of soluble metal phenoxides as additives. Additional work is required due to the formation of precipitates of the additives or their degradation products during the course of high temperature testing.

5. Gas Bearings. Gas lubricated foil bearings have significant promise because of their ability to easily accomodate the requirements associated with extreme temperature, high-speed shaft support systems which are typical of future turbine engine designs. Some other advantages derived from their application are: (a) the elimination of lubricant supply and cooling components (weight savings), (b) virtually no viscous drag to impair cold starting, and (c) no lubricant starvation failures due to oil leakage and evaporation or attitude of the system. However, extensive development is still required before gas lubricated foil bearings can be routinely applied to the rotor support systems of main propulsion systems.

6. The most immediate potential for application of gas bearing technology is in the small gas turbine power plants where bearing loads are relatively light such as in cruise missiles, auxiliary power units and direct lift engines.

7. Ester-Based Lubricants. Improvement in the bulk oil thermal oxidative stability of ester-based lubricants is necessary for the lubrication of future high energy-density propulsion systems. Preliminary chemical analysis and the application of simple kinetics show that additive chemistry, reaction rates, interactions and reaction products provide the basis for studies for making such improvements. Such work is of a broad enough scope that it would best be conducted under a separate program involving ester-based lubricants only.

RECOMMENDATIONS

1. Improvements in the thermal oxidative stability of ester-based lubricants should be continued. The major objective of such a program should be to meet the lubrication needs of anticipated high energy-density aircraft propulsion systems.
2. The development of gas lubricated compliant bearing technology should be pursued in a step-wise approach starting with near-future practical objectives, such as rotor support systems for auxiliary power units and cruise missile engines, and leading to the shaft support of aircraft main propulsion systems.
3. Due to the long lead times required for developing new lubricants, such as polyphenyl ethers and fluorinated ethers, a low level effort should be pursued in this area.

ANALYSIS OF RESULTS AND DISCUSSION

1. Assessment of Technology and Requirements. The environment of the lubrication system is affected by many individual factors related to engine performance and design as well as to aircraft mission. Although much can be done to "protect" the lubricant from this environment by well planned thermal management, the ultimate factor in the process is the available

heat sink. Heat from the lubrication system is usually rejected to the atmosphere (air/oil cooler) or to the fuel (fuel/oil cooler). However, as Mach number of the aircraft increases, the capacity of these heat sinks decreases. In fact, after a certain point, due to ram air heating, the oil system gains heat from its surroundings. In the early stages of this program, much attention was being given to Navy aircraft designs capable of Mach 3+ operation. Because of the limiting effect that higher Mach numbers have on available heat sink, Mach number was chosen as the parameter on which to base estimates of the maximum bulk stream temperature of the lubricant. The maximum bulk stream temperature was then considered as the basis for designating the type of lubricant chemistry or lubrication system required. Based on an extensive review of available literature and related research efforts (references 2 to 9 inclusive) bulk oil stream temperatures were estimated for engine performance at various aircraft Mach numbers. The estimates were made for present state-of-the art thermal management and for optimized thermal management. These estimates are shown plotted on Figure 1. The space between the two thermal management characteristic lines would be the range of expected bulk stream temperatures at a given Mach number. The literature also shows that based on computer-model thermal analysis severe weight penalties or reliability/maintainability problems would occur if lubricants which meet these temperature capabilities are not available prior to the design of the propulsion system. Also shown in Figure 1 are the lubricants or bearing support systems which are considered the most practical to withstand the environment. These selections were made on the basis of a review of lubrication literature and prior NAPC efforts in lubricant research (references 10 to 15 inclusive).

2. The ester based lubricants (appearing at the lower end of the curves of Figure 1) are the common gas turbine engine lubricant in use today. Virtually all U. S. military and commercial aircraft engines operate on ester lubricants. These fluids consisting of an ester basestock and an additive package consisting primarily of oxidation inhibitors, metal passivators and load carrying agents, are readily available, relatively inexpensive and perform quite satisfactorily. However, at sustained flight above Mach 2.5, it is apparent from Figure 1 that the current ester technology is approaching its limit in an oxidizing environment. At these conditions new ester technology would have to be developed, inerted ester systems would have to be considered (see max. capability listings on Figure 1) or lubricants based on polyphenyl ethers would be required. Research with ester structures and additive chemistry can possibly extend ester capability to 246°C (475°F) thus permitting use of esters in aircraft capable of operation up to Mach 2. Inerting of the lubrication system could extend the range of ester lubricants to Mach 2.7 - 4+ operation.

3. Polyphenyl ether (PPE) based lubricants have already been used for operation above Mach 3. The J58 engine of the SR71 aircraft has been operating on Monsanto Skylube 600 (a PPE based lubricant) since its introduction into service. PPE fluids are very costly and their high viscosity

at low temperature compromise or complicate engine start-up in colder climates. Also, research on PPE fluids is being directed at raising their maximum bulk temperature capability from 316°C (600°F) to 371°C (700°F).

4. The fluorinated ethers would be the next type of chemistry sought to resist the more hostile environment as Mach number increases and bulk stream temperature exceeds the PPE capabilities. Fluorinated ethers are extremely expensive with little potential for a reasonable price structure even when produced in quantity. One of the drawbacks of using fluorinated compounds is the formation of hydrofluoric acid as a result of decomposition. Hydrofluoric acid is extremely corrosive and, therefore, introduces a very difficult metallurgical problem to the engine designer.

5. The uppermost portion of the plot of Figure 1 shows a region where gas bearings are listed instead of a lubricant. Such "bearing systems", which use air as the lubricant, circumvent the typical problems associated with liquid lubricants, i.e. thermal decomposition, high viscosity at low temperatures, cost, etc. The technology to design small lightly loaded gas lubricated foil bearings is well developed. There is much to be done before such technology can successfully be applied to the support of the main rotors of gas turbine engines.

6. Although the curves of Figure 1 are based on Mach number considerations, the temperature - lubricant information presented is also applicable to special engines which operate at higher than normal oil temperatures irrespective of aircraft Mach number. For the small high energy-density engines, such as those used in cruise missiles, direct lift applications and some advanced auxiliary power units, space and weight considerations can preclude the use of some of the thermal management techniques used in larger engines. Therefore, temperatures are likely to be very high in such engines although Mach numbers are relatively low or not applicable. From the reviews of plans and analyses of typical small high energy-density engines, it is estimated the maximum bulk oil stream temperature will be in the order of 246°C (475°F) to 260°C (500°F).

7. Liquid Lubricants - Research Effort for High Mach Advanced Aircraft. At the start of this program, the Navy's advanced fighter/attack plans included aircraft with cruise capability in excess of Mach 2.5. For this reason, referring to Figure 1, it can be seen that liquid lubricant research would be directed to the polyphenyl ethers, the fluorinated ethers, and the inerted ester systems. The initial stages of the effort to investigate the performance of this type of lubrication included experiments with the equipment and procedures required to perform testing at extremely high temperatures. Much of the effort was concentrated on modifying existing lubricant evaluation testers and procedures, procuring candidate test fluids and performing baseline tests. However, during this phase of the program the Navy's plans for future aircraft requirements shifted emphasis to maximum cruise speeds of Mach 2.2. The research efforts on the extreme

temperature lubrication systems could no longer be justified by a future Navy aircraft requirement. Therefore, this concept was terminated in its early stages. Although incomplete, these efforts did generate significant information.

8. Inerted Ester Systems. Current ester based lubricants operating in an environment abundant with air are limited by their oxidative characteristics to about 204°C (400°F) to 218°C (425°F). In the absence of oxygen the breakdown of the ester would be by the mechanism of pyrolysis or thermal fracturing of the molecule. Inerting of engine lubrication systems would permit operation at temperatures approaching the ester basestock thermal stability (pyrolytic) limit which is significantly above (66°C (150°F)) its oxidative stability limit. The effects of inerting or limiting the oxygen available to a lubricant during thermal stressing were the object of the early investigations under this program. The testing was performed on a lubricant that was typical of the current ester lubricant technology as required by specification MIL-L-23699 (reference 16). This is the current lubricant specification used for Navy gas turbine aircraft engines. The test apparatus and procedures for the inerted testing were similar to those used for oxidation testing under MIL-L-23699C except that no catalytic metals or condenser were used. Essentially, the test consisted of blowing mixtures of nitrogen (N_2) and oxygen (O_2) through the test oil at various temperatures. The test conditions for this investigation are shown below:

Time	-	72 hours
Temperature	-	Variable (204°C (400°F) - 288°C (550°F))
Humidity	-	Dry
Sample Volume	-	100 ml
Gas Flow Rate	-	250 ml/min.
Gas Mixture	-	Variable (0 - 21% Oxygen in nitrogen)

After testing, test oil performance was assessed by measuring viscosity change, total acid number (TAN) change and evaporation loss.

9. The first tests were performed at 204°C (400°F) while varying the O_2 content of the blown gas from 0 to 21 percent, i.e., from pure N_2 to air. The results for viscosity change, TAN change and evaporation loss versus O_2 content of blown gas are shown on Figures 2, 3 and 4 respectively. Results for the oil sample stressed in air (21 percent O_2) were typical of what one would expect of a MIL-L-23699C oil when subjected to such environmental conditions. At the lower O_2 levels, changes in properties occurred to a somewhat lesser extent and there were no deleterious effects, e.g., viscosity loss due to pyrolysis. During the second series of tests, at 232°C (450°F), the oil solidified in the presence of air (21% O_2). This result also was expected since experience with this type of oil indicates that its oxidative stability limit is between 204°C (400°F) and 218°C (425°F).

10. Examination of Figures 2 and 3 shows that viscosity and TAN experienced a breakpoint between 1.2 and 2.2 percent O₂. At the same point, evaporation rate made a significant increase (Figure 4). Above that O₂ level, degradation proceeded at a very rapid rate to the extent that the lubricant solidified in the 21 percent O₂ test. Using 25 percent viscosity change as a criteria for acceptable performance (based on MIL-L-23699 experience) it is apparent that for operation above 232°C (450°F), it is essential to keep the O₂ level below one percent. Figure 2 also shows that at 288°C (550°F) and with pure N₂ as the blown gas, the viscosity change is well above the 25 percent level. From this result it appears that the extension of ester lubrication to 302°C (575°F) by inerting (see Figure 1) is not possible.

11. Since the additives used in ester based lubricants are primarily anti-oxidants it was decided to investigate the performance of a typical ester lubricant basestock under inerted conditions. The results of this testing are shown in Figure 5. Baseline data generated for the basestock stressed in air are also included. Note that comparing the results for air oxidation of Figures 2 and 5, severe degradation (change in viscosity greater than 50 percent) occurs at a much lower temperature with the basestock than with the fully blended lubricant (149°C (300°F) vs 204°C (400°F) respectively). Inerting of the basestock test with 100 percent N₂ reduced the degradation to the same order of magnitude as occurred with the inerted tests of the blended oil (Figure 2) at 232°C (450°F) and 260°C (500°F). It appears from these data that the additive package is unnecessary with an inert environment. However, it must be kept in mind that although excellent resistance to degradation was achieved in this case with an uninhibited ester this test was performed in glassware with no catalytic metal present.

12. Because of the extremely high temperatures used in the inerted testing it was considered that evaporation may play a role in the viscosity change. Therefore, some additional testing was performed on the basestock. For this testing, the test apparatus was equipped with a condenser to reflux the vented products back into the tube holding the bulk of the oil. The baseline run with air showed a slight improvement over the non-reflux test in air (see Figure 5). However, the viscosity changes still indicated very severe degradation of the fluid. In the case of the inerted test, Figure 5 shows that with refluxing it becomes possible to control degradation in the 288°C (550°F) to 316°C (600°F) range.

13. The next step in the evaluation of esters in an inerted environment was to perform testing under dynamic conditions which would simulate the lubrication system of a gas turbine engine. This was accomplished in the High Temperature Deposition (HTD) tester which is described in detail in reference 13. The HTD test simulates the basic parameters that influence deposition and oil degradation throughout typical gas turbine engine lubrication systems. The test conditions applicable to this program are shown as follows:

Oil-In Temperature - 232°C (450°F) 260°C (500°F)
Lower Deposition Tube Temp - 343°C (650°F)
368°C (695°F)
Environmental Temperature - 177°C (350°F)
Gas - 0, 1, & 21% Oxygen in nitrogen/oxygen mixture
Gas Flow Rate - 1000 ml/min \pm 15 ml/min
Initial Oil Change - 250 ml \pm 20 ml
Test Duration - 6 Hours

14. Testing was performed on a typical MIL-L-23699 ester lubricant base-stock. The results of tests performed with the HTD tester are shown on Figure 6. Baseline data, where air is the injected gas, show very severe fluid degradation as indicated by the very high viscosity changes at 232°C (450°F) and 260°C (500°F) oil temperatures. Comparing these values to those obtained in the glassware test discussed previously (and also shown on Figure 6), the degradation is at the same severity level, although the HDT test was run at much higher oil temperature. Perhaps the relative oil/air quantities (250 ml/1000 ml/min. and 100 ml/250 ml/min. for the HTD and glassware tests, respectively), materials contacted or test durations account for this difference. When the HTD test was conducted with reduced O₂ (99 percent N₂ + 1 percent O₂) gas injection there was a significant decrease in degradation. Another significant decrease was accomplished when the injected gas was 100 percent N₂. However, in neither case did refluxing of vent materials offer any further improvement. This phenomenon does not agree with the glassware test results shown on Figure 5. A possible explanation may be the relative efficiencies of the condenser systems employed for the refluxing. However, the extremely low viscosity changes obtained for the 100 percent N₂ systems are encouraging with regard to a goal of maintaining stable lubricant performance at 302°C (575°F) in an inert environment.

15. From the data analyzed and considering that experience indicates that a reasonable limit for viscosity change is 30%, it appears that inserting of ester based lubricants can raise their operating regime to a range of 302°C (575°F) to 316°C (600°F). However, certain points of concern must also be noted: (a) At such temperatures the ester fluid is above its flash temperature, (b) To take full advantage of the capabilities of an inerted system, virtually all oxygen must be excluded from and kept from entering the lubrication system, (c) Venting of lubricant vapors overboard must be avoided, (d) The lubricating ability of the oil may be impaired in either very low or zero oxygen environments. The concern over lubrication capability is supported by the fact that when a N₂ inerted test was attempted in the High Temperature Bearing Test (conditions of reference 16) the test was terminated due to bearing failure. The failure was analyzed as a lubrication

failure. Although only one test was attempted, the results were considered significant since it is the only bearing failure experienced in 150 High Temperature Bearing Tests run at NAPC.

16. As a final precaution concerning the data generated under inerted conditions, it must be kept in mind that none of the tests were conducted in the presence of catalytic metals.

17. Polyphenyl Ether. As seen from Figure 1, polyphenyl ethers which are considered oxidatively stable to 275°C (527°F) uninhibited, are strong contenders of potential interest as high temperature aircraft turbine engine lubricants. Monsanto Skylube 600, which is an inhibited polyphenyl ether, is the only lubricant qualified (reference 17) to operate in the J58 engine (SR71 Mach 3+ aircraft). However, at the time this assignment was initiated, the Naval Research Laboratory (NRL) had been conducting research to further extend the capabilities of polyphenyl ether lubricants. It was reported by NRL (reference 18) that polyphenyl ethers, in the presence of basic salts of the alkaline metals and of barium, are stable to 330°C (626°F) and for short periods to 371°C (700°F). Also reported is the fact that these inorganic salts are insoluble in the polyphenyl ethers, and the unreacted excesses must be removed by filtration after reaction at the elevated temperatures required by the processing treatment. In an attempt to simplify the stabilization procedure, a series of polyphenyl ether - soluble metal phenoxides was synthesized, and their effectiveness was evaluated under laboratory (glassware) oxidizing conditions (reference 19). In general the results were comparable to those with the inorganic salts. The formulation chosen for further evaluation consisted of polyphenyl ether--bis m-(m-phenoxyphenoxy) benzene containing 0.3 wt. % of barium m-(m-phenoxyphenoxy) phenoxide.

18. As a follow-on to the laboratory analysis NAPC and NRL cooperated in a joint effort to conduct an engineering evaluation of the NRL stabilized polyphenyl ether in dynamic lubrication system simulators. The plan was to conduct screening tests in the High Temperature Deposition Test (described in reference 13) followed by a final evaluation in the High Temperature Bearing Deposition Test (reference 20) which simulates a full scale engine bearing compartment and lubrication system. Both of these test methods and equipment were developed to evaluate ester based lubricants. Therefore, considerable development work was necessary to arrive at procedures necessary to evaluate the polyphenyl ether lubricants at meaningful conditions. For the High Temperature Deposition Test, the Monsanto Skylube 600 was used in a series of tests to establish the conditions at which to run the NRL experimental polyphenyl ether lubricant. Because of the large volume of oil required and because of the very high cost of Skylube 600, test development on the High Temperature Deposition Tester was conducted on ester lubricants. Test periods were kept as short as possible to reduce ester lubricant degradation while establishing the conditions necessary to evaluate the polyphenyl ether fluids.

19. The results of the more significant Skylube 600 tests on the HTD Tester are given in Table I. From these data it is apparent that the breakpoint of the Skylube 600 occurs in tests where the oil-in temperature exceeds 288°C (550°F) and the maximum surface temperature exceeds 427°C (800°F). From these data it was decided to evaluate the NRL fluid at an oil-in temperature of 302°C (575°F) and a maximum surface temperature of 441°C (825°F). Unfortunately due to the large volume of oil needed to conduct the final development test in the High Temperature Bearing Deposition Tester there was not a sufficient quantity of the Skylube 600 remaining to run a HTD test at these conditions. Therefore, the only baseline used for evaluating the NRL inhibited polyphenyl ether lubricant was the performance of its basestock at the same conditions. The test results for this evaluation are given in Table II. Observation of the data shows that deposition and viscosity change are low compared to these values for the basestock. However, the 99.9 percent viscosity rise is still considered high and is indicative of the need for further research efforts. It was also noted during the course of this test that a cloud formed in the oil reservoir. NRL determined that this cloud was due to some precipitation of the additive or its degradation products. These findings certainly indicated the need for additional work in this area. However, the program emphasis was changed to fluids required for lower temperature operation and no further studies were made under this project. A follow-on effort at a much lower priority level is being conducted under reference 21.

20. Although the testing did not proceed to the evaluation of the NRL fluid in the High Temperature Bearing Deposition Test, this test was performed on the Skylube 600. The results of this test are reported in Table III. For comparative purposes the conditions and results for the polyphenyl ether test are compared to the conditions and specification limits for the currently used aircraft engine oils (MIL-L-23699). It can be seen from Table III that the performance characteristics of the Skylube 600 are poor compared to the acceptance limits for the MIL-L-23699 oils (which are evaluated at much lower temperatures). These are the results that were desired from this test. Because the Skylube 600 test was a baseline, conditions were chosen to produce poor performance results as measured by MIL-L-23699C standards. The performance of experimental polyphenyl ether lubricants would then be expected to be better than those for the Skylube 600 and at least close to the MIL-L-23699C limits.

21. Gas Bearings. The third and final area of consideration under this program for extreme environments of gas turbine engine lubrication systems was the gas lubricated bearing. Gas bearings, which use air or some other gas such as the working fluid of the particular equipment, had been used for several years in very lightly loaded applications, e.g. dental drills, grinding spindles and tape transports. As the technology advanced and

computer aided design criteria were developed, the application of gas bearings became more feasible to other areas. First among these which were related to aircraft systems were the support bearings of the environmental control systems (e.g. F-4, A-7, B727 cooling turbines and DC-10 air cycle machine). Soon interest turned to the main propulsion systems since the successful application of such bearings would eliminate or significantly reduce many of the problems inherent in designs employing liquid lubricants and rolling element bearings. This advantage is particularly applicable to very high speed aircraft engines and to systems where the trend is for more power out of smaller and lighter packages. Under these circumstances, lubricant temperatures and main shaft bearing speeds become extremely high. Gas bearing operating temperatures possible with today's technology far exceed even the projected capabilities of liquid lubricants. With a gas bearing, there is no thermal stability limit on the "lubricant" which will most likely be air. A bonus is derived from the fact that the viscosity of air increases with increasing temperature resulting in a gain in the load carrying ability of the bearing at higher temperatures. Additionally, the speed capabilities of gas bearings are virtually limitless whereas reliable operation of rolling element bearing at speeds in excess of 2.5 million DN is extremely difficult to achieve.

22. As a first step in investigating gas bearings for Navy aircraft applications, an extensive review was made of the literature and government contracted efforts dealing with the development of related technology (references 14, 15 and 22 to 31). Pertinent meetings and contract reviews were also attended. Aside from confirming the initial potential advantages foreseen in the development of gas bearing technology for aircraft propulsion systems, the following general advantages were also observed:

- a. Thermal management problems are reduced because bearing heat generation is very small compared to rolling element bearings.
- b. Pumps, filters, tanks, seals, etc. are eliminated. The problems of scavenging a liquid lubricant from sumps at all shaft attitudes is eliminated.
- c. There is no low temperature restriction due to the viscosity of the lubricant.
- d. There are no lubricant-engine hardware material compatibility problems.
- e. There is no danger due to spontaneous ignition of the lubricant.
- f. There are no problems associated with the loss of lubricant due to leakage or evaporation.

g. There are no lubricant qualification, quality assurance, purchasing or logistic expenditures.

23. Accordingly it was concluded that it would be beneficial to participate in the development of gas bearings for the main shaft support of gas turbine engines. At this time a fairly new concept, the compliant gas bearing, was receiving much attention. Of particular interest was a design known as the gas lubricated foil bearing. The development of this technology although not strictly lubricant technology, was selected as an area to be pursued during the course of the NAPC lubrication concepts program.

24. Foil bearings, because of their compliancy, appeared to be able to overcome many of the problems associated with other type gas bearings. Small scale foil bearings had considerable flight experience in the cooling turbine of the F4 aircraft and air conditioning equipment in the DC10 and B727 commercial aircraft. Excellent reliability had been reported for these applications. Although these bearings were quite small compared to what would be required for main shaft bearings, the prospect of increasing the capacity of the foil bearing looked good. An Air Force program had already demonstrated the feasibility of using foil bearings in the main rotor shaft of a small gas turbine engine (reference 24). The next step in their program was to apply foil bearings to a 1000 to 3000 pound thrust engine. This thrust class was chosen as the next reasonable step in developing the technology and experience necessary to eventually attain success in large scale jet engines.

25. Most of the above discussion has been directed toward the application of gas bearings to engines in which conditions are such that the application of liquid-lubricants and rolling element bearings would be extremely difficult, if at all possible. There are, however, more immediate applications where the use of gas bearings, although not mandated by the environment, can simplify the design. Small expendable or short life engines can benefit greatly from many of the advantages of gas bearings discussed previously. Since the number of starts of these engines is small, one of the major problems encountered in the development of foil bearings (providing sufficient anti-wear properties between initial shaft rotation and "lift off" of the shaft from the bearing) is minimized. Therefore, it was also noted that a program to develop foil bearing technology applicable to the main rotor of an expendable turbine engine would be one which would result in the most immediate application in service.

26. Considering the above rationale and after reviewing an ongoing Air Force contract (reference 23) to develop gas lubricated foil bearing technology for small gas turbine engines, it was decided that participation in this effort would be beneficial to the development of future Navy aircraft and missile propulsion systems. Therefore, in January 1975, NAPC issued a Military Interagency Purchase Request (MIPR), reference 33, to

the Air Force and thus became a participant in this effort. This followed earlier Army involvement and funding under this contract. Therefore, this development program became a coordinated Air Force/Army/Navy program.

27. The overall objective of the program was to extend and demonstrate the state-of-the-art of gas lubricated compliant surface bearings to 1000 to 3000 pound thrust-class full scale turbomachine requirements and constraints. Briefly the planned approach was as follows:

- a. Establish loads imposed on journal and thrust bearings by selected turbomachine.
- b. Apply existing or where necessary develop the analytical design tools required for bearing development.
- c. Design, fabricate and develop test rigs for testing and development to meet the selected turbomachine requirements while subjected to the maneuvers of MIL-E-5007C.
- d. Conduct a base material and coating selection and evaluation program to select materials that would meet the temperature requirements of the thermal analysis.
- e. Develop thrust and journal bearings to achieve the load capacity, high temperature and other turbomachine application requirements.

28. The NAPC participation in this program was directed primarily toward the material screening and selection phase of the contracted effort. Since at this time the NAPC target was for lubrication in extreme temperature environments, it was felt that support in the high temperature materials area would best support this goal.

29. The gas-lubricated foil bearings that formed the initial basis for this effort were of a design patented by the Garrett Corporation. General design of these bearings is shown in Figure 7. The design characteristics of this bearing are such that at operating rotational speeds the journal or thrust plate "rides" on a film of air that is generated hydrodynamically by the motion of the rotating element. At operating speed, the rotating member does not touch the foils. However, at start-up and shut-down, prior to the development of hydrodynamic pressure sufficient to support the shaft load, the rotating member (journal or thrust plate) is in contact with the foils. Since the foils are very thin, they provide very little heat sink and temperatures can become extremely high. For this reason, careful materials development and selection for both the substrate material and the coating material is an essential phase of achieving successful operation of the bearing.

30. The materials development activities of the contracted effort (reference 32) resulted in the demonstration of three substrate alloys capable of

meeting foil bearing strength, modulus of elasticity and oxidation resistance requirements to temperatures of 649°C (1200°F). These materials are Inconel X-750, Inconel 718 and Haynes 25. The evaluation of low friction, oxidation resistant coatings for foils resulted in the acceptance of several materials. The most successful among these were B₄C, TiB₂, Cr₂O₃ and TiC. Although these coating materials were considered acceptable with respect to lubricative wear, oxidative resistance and substrate compatibility properties, they were not optimized for processing and application to the substrate. Despite these advances towards achieving materials capability at 649°C (1200°F), the chance of success of the overall program was clouded by the thermal analysis of the engine which indicated that the foil bearing operating temperature trends at 50,000 feet altitude will exceed these foil materials and coatings capability. However, the validity of this analysis was not checked by actual foil temperature measurement.

31. The materials evaluation phase of this program as well as all other phases of this program are discussed in detail in the final contract report (reference 34). Although the successful demonstration of foil bearings in a 1000 to 3000 pound thrust class engine was not achieved, the program did significantly advance the materials, analytical and testing technology needed to improve foil bearing capacity for gas turbine engine applications.

32. The gas bearing effort participation under this program has led to several conclusions with respect to their application to Navy air propulsion systems. Foil lubricated gas bearings technology requires extensive additional development, if such bearings are to find their way into aircraft propulsion systems. However, the recent progress made in this area, especially with the compliant bearings, indicates that the Navy can benefit from future support of development programs. The most immediate potential applications for this technology appear to be in the small gas turbine power plants where bearing loads are relatively light as in cruise missiles, auxiliary power units, and direct lift engines. In addition to the many advantages listed above, the inherent corrosion resistance of the gas bearing materials and the absence of a liquid lubricant of unknown long term storage stability characteristics make this type of bearing especially attractive to the cruise missile engine. In summary, it is believed that the Navy will benefit from future support of compliant gas bearing programs.

33. Ester Lubricant Studies. When the emphasis for future Navy weapons systems made a transition to V/STOL aircraft and cruise missiles vice high Mach aircraft, it was decided to revise the original planning of this program as related to lubrication concepts and redirect the major effort toward the development of ester lubricant technology. Improvement in the bulk oil thermal oxidative capabilities of esters were judged to

be a viable area for studies related to the high energy-density propulsion systems required for V/STOL type aircraft and cruise missiles. This phase of the effort was initiated as a joint NAPC-NRL effort. NAPC performed the engineering testing and evaluations while NRL was responsible for the chemical analysis. After completing the preliminary phase of this investigation, it was decided to continue this work under a new assignment (reference 21). This administrative change was made because of the significant departure of the revised program from the original objectives.

34. The results of the preliminary phase of the ester improvement work were reported by NRL in reference 35 which is also included as Appendix A to this report. Basically, this work consisted of analysis of the results of a large number of HTD tests conducted on a "model" ester lubricant. This model consisted of a very simple ester basestock and two typical antioxidants, phenyl-alpha-naphthylamine (PANA) and dioctyldiphenylamine (DODPA). Details of this investigation are given in Appendix A. However, a summary of the findings is given below.

35. Using simple kinetics as applied to an inhibited lubricant, a mathematical expression was developed to relate the induction (period of relatively low rate of oxidation) time of the lubricant to the original concentration of the oxidation inhibitors PANA and DODPA. When compared to actual results for the models having only one of the inhibitors, the induction times predicted by this expression matched very closely to real induction times. However, agreement to real data was not as close when the expression was used to predict induction times for models containing both inhibitors. Actual induction times were always less than predicted. Interaction of the additives was therefore suspected. This suspicion is supported by the fact that analysis of samples from tests involving both additives revealed several compounds that did not form when the additives were used separately in the base ester.

36. In an investigation to determine the "fate" of the antioxidants after the model ester lubricant was stressed under several different conditions, it was found that regardless of the stressing conditions (variable oil and surface temperatures and test duration), the additives and/or their reacted products were not lost due to evaporation. This conclusion was drawn from the fact that regardless of the amount of additives analysed to be in the lubricant (from 1.0 percent to virtually 0 percent) the nitrogen content (present only as a result of the additive) remained nearly constant. It was assumed that the nitrogen represented that present in the additives as well as in oxidized additive compounds. The role of the reacted additive compounds in the process of inhibiting oxidation has not yet been determined. Future efforts under this program included plans to identify individual oxidation products to provide clues as to their roles in the ester inhibition process.

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37. As mentioned previously, for administrative purposes this assignment was terminated before completion of the ester improvement phase. This work is being continued under reference 21.

**FIGURE 1. LUBRICATION REQUIREMENTS FOR BULK STREAM
TEMPERATURES ESTIMATED AT VARIOUS
AIRCRAFT MACH NUMBERS**

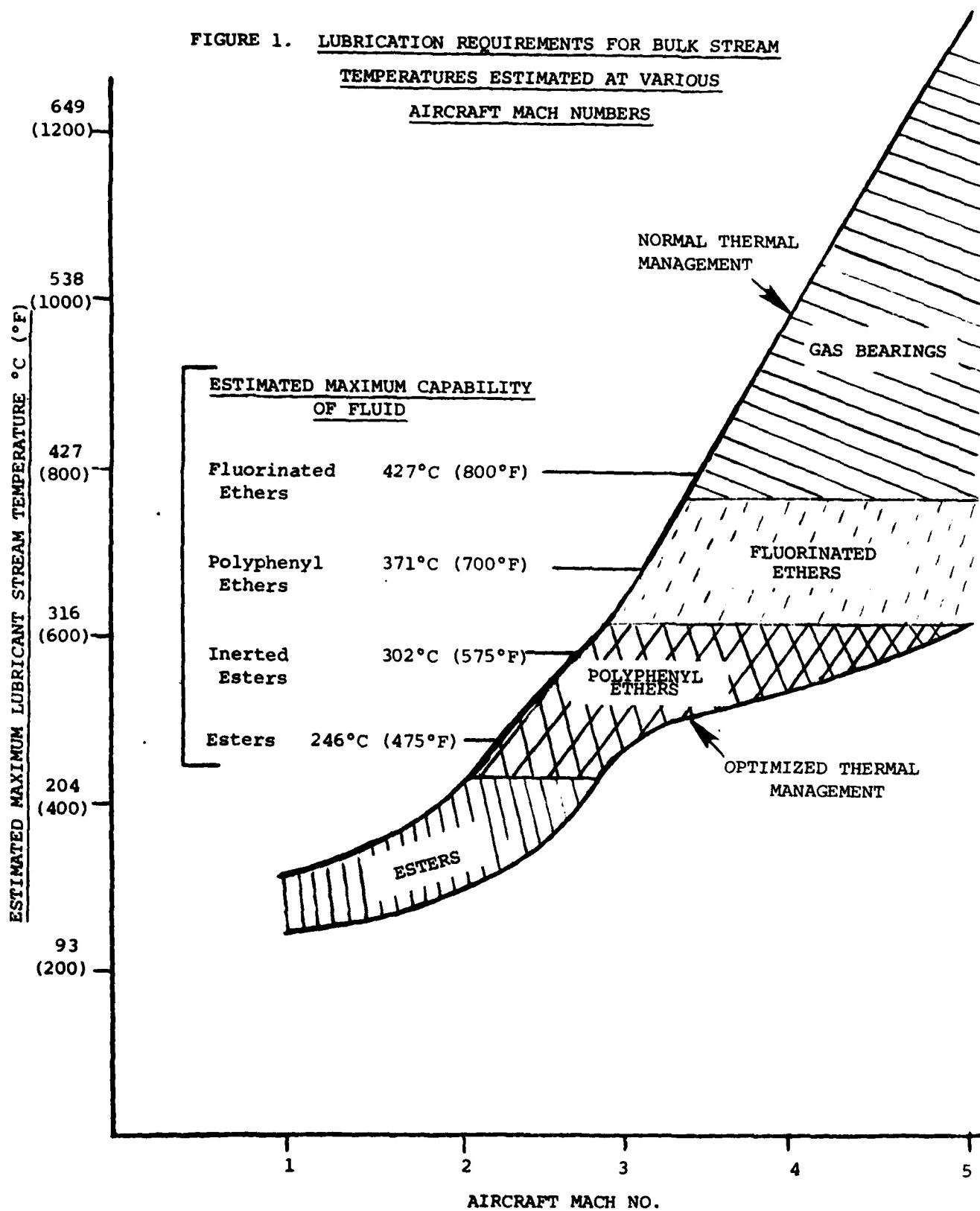
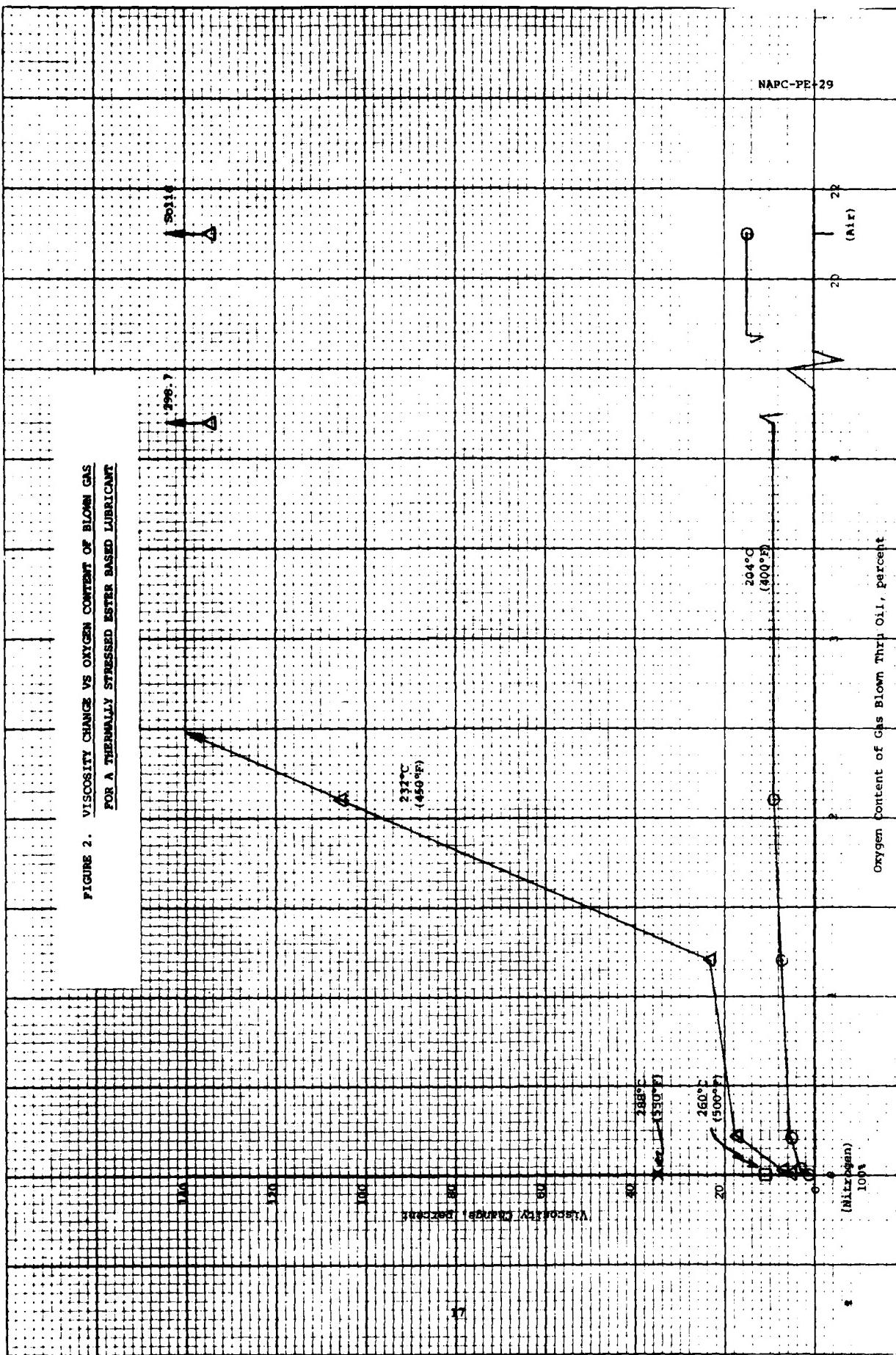
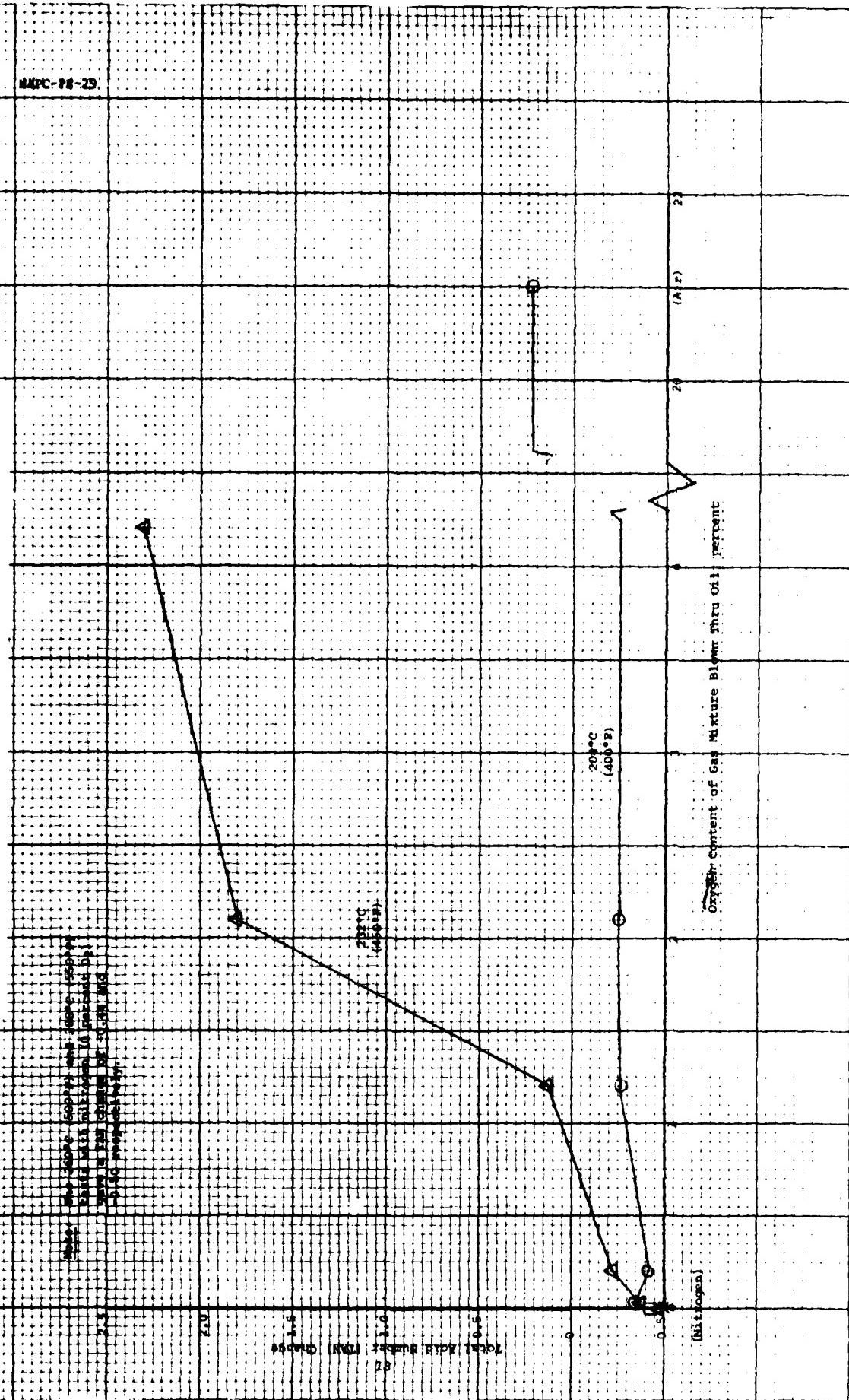


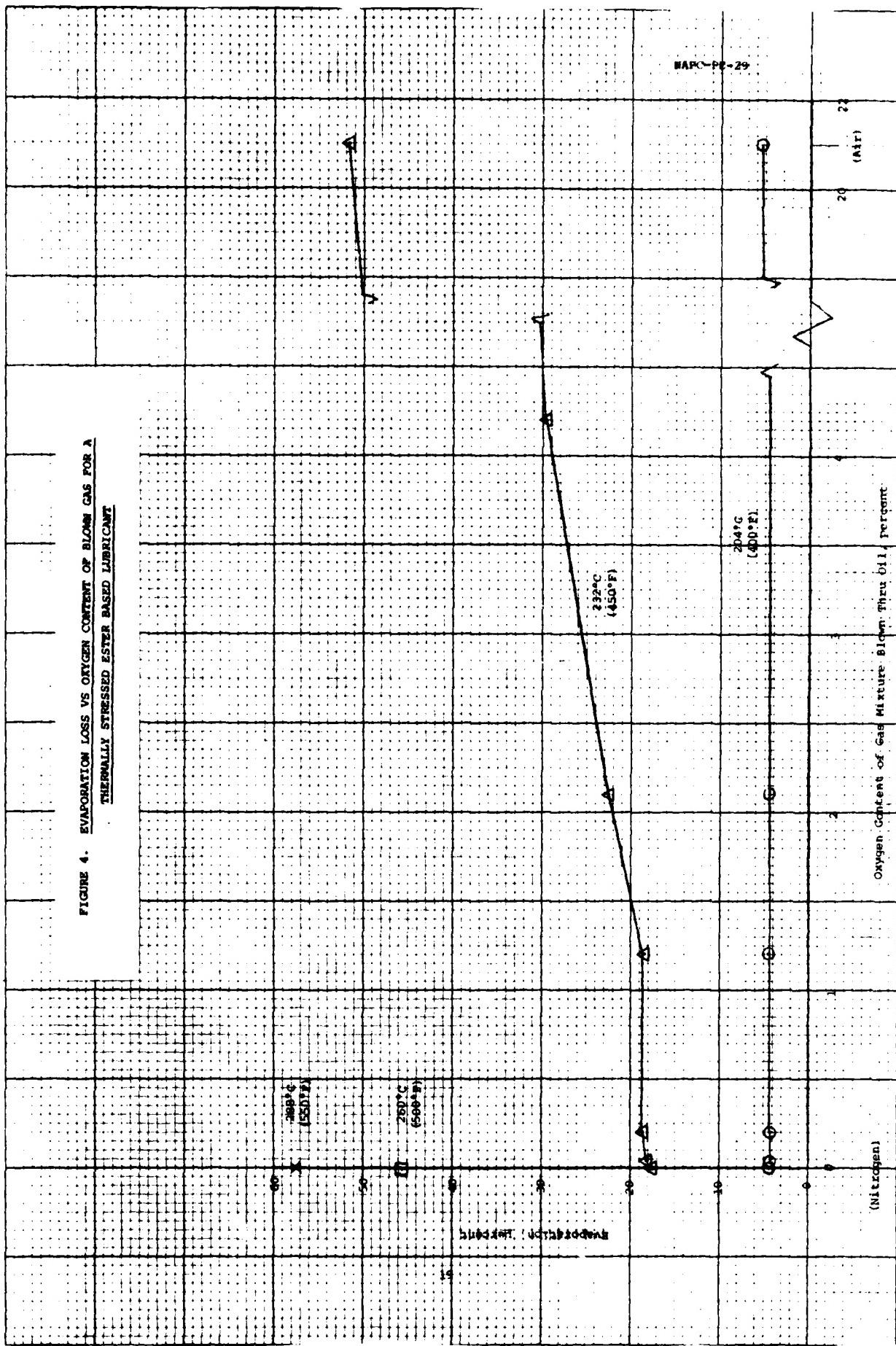
FIGURE 2. VISCOSITY CHANGE VS OXYGEN CONTENT OF BLOWN GAS
FOR A THERMALLY STRESSED ESTER BASED LUBRICANT



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FIGURE 3. TAN CHANGE VS. OXYGEN CONTENT OF BLOWN GAS
FOR A THERMALLY STRESSED ESTER BASED LUBRICANT





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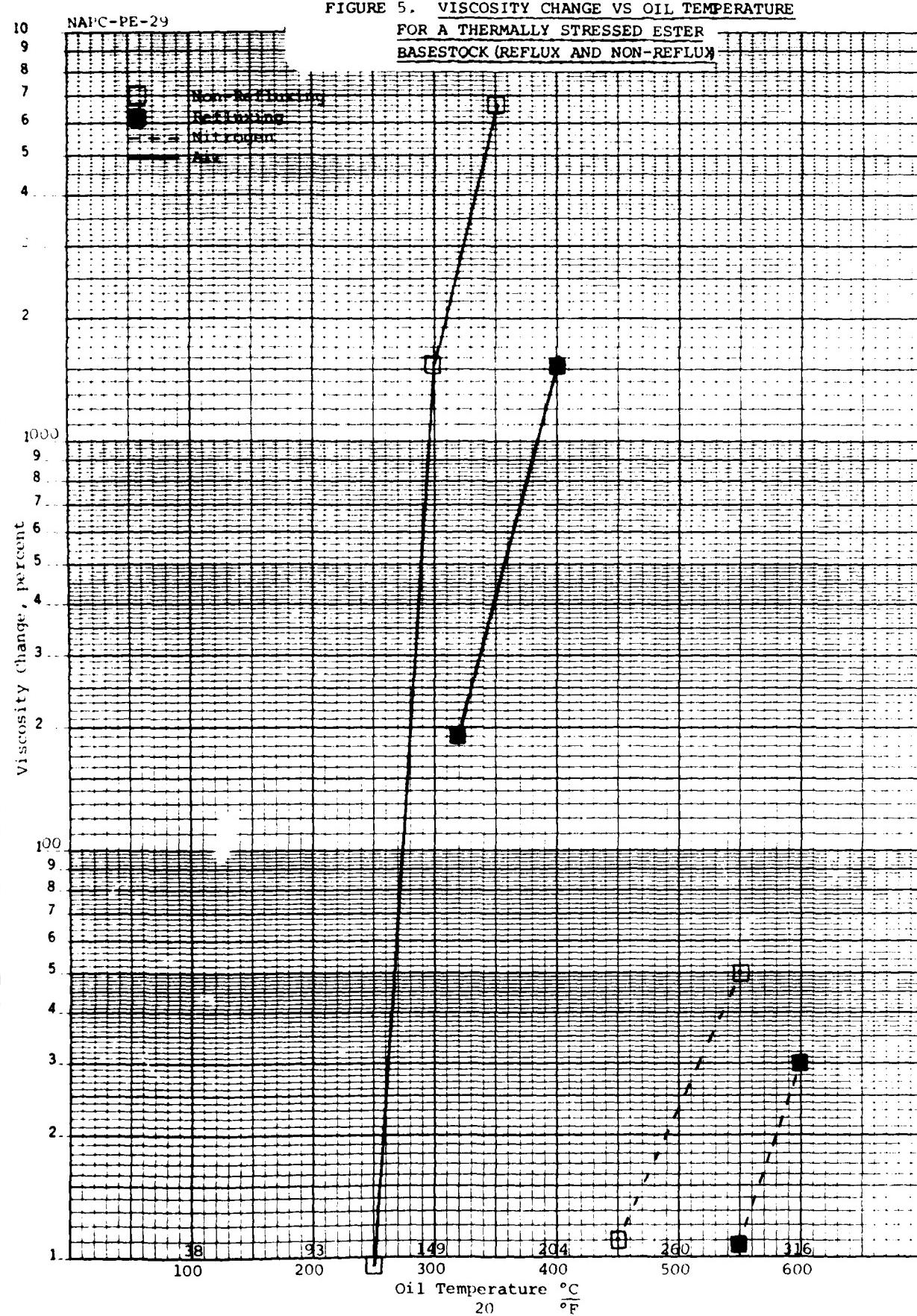
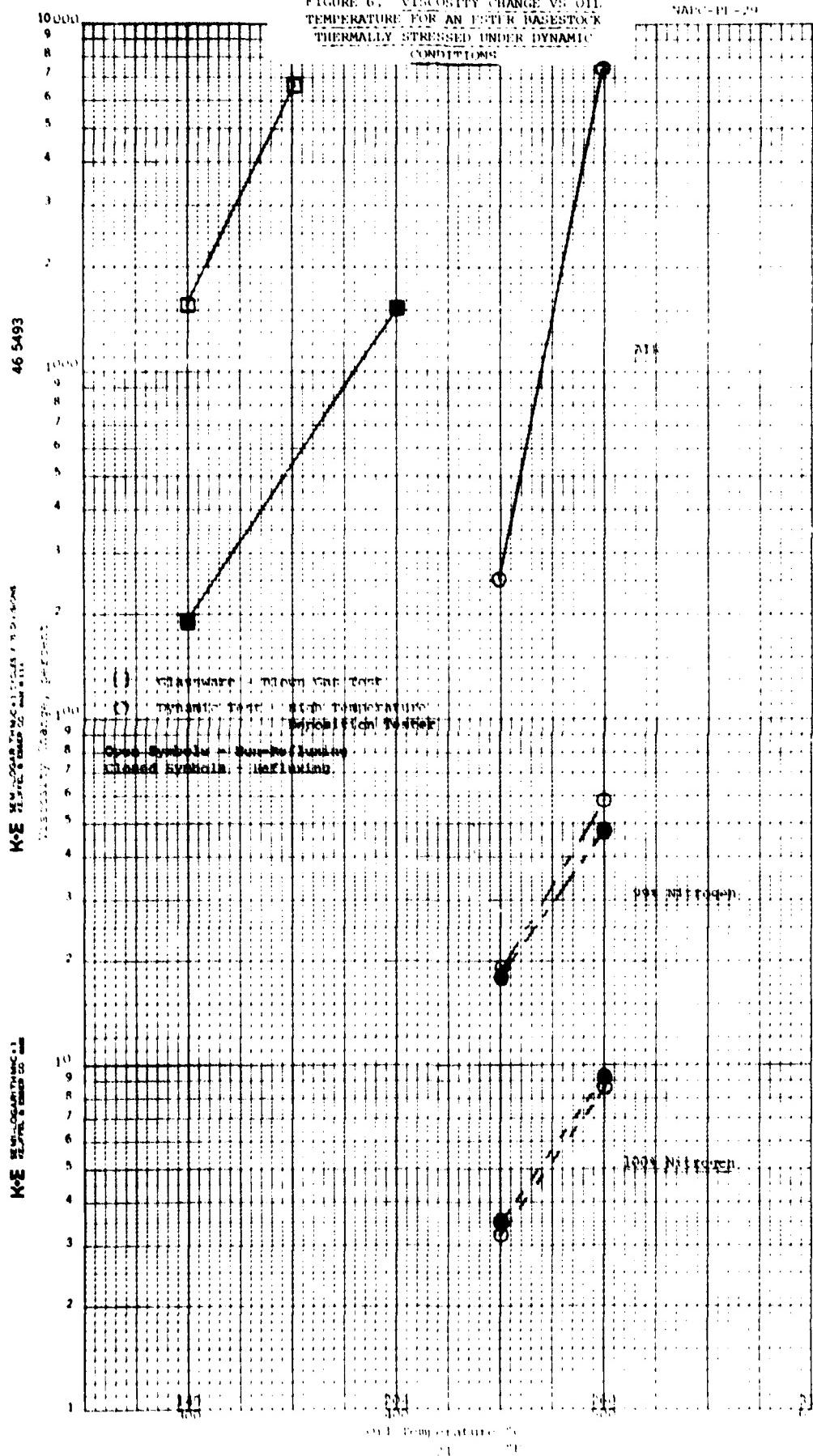


FIGURE 6. VISCOSITY CHANGE VS OIL TEMPERATURE FOR AN ESTER BASESTOCK THERMALLY STRESSED UNDER DYNAMIC CONDITIONS

WAN-PI - 14



THE SELF ACTING COMPLIANT FOIL BEARING CONCEPT

FIGURE 7. THE SELF ACTING COMPLIANT FOIL BEARING CONCEPT (THE GARRETT CORPORATION PATENT)

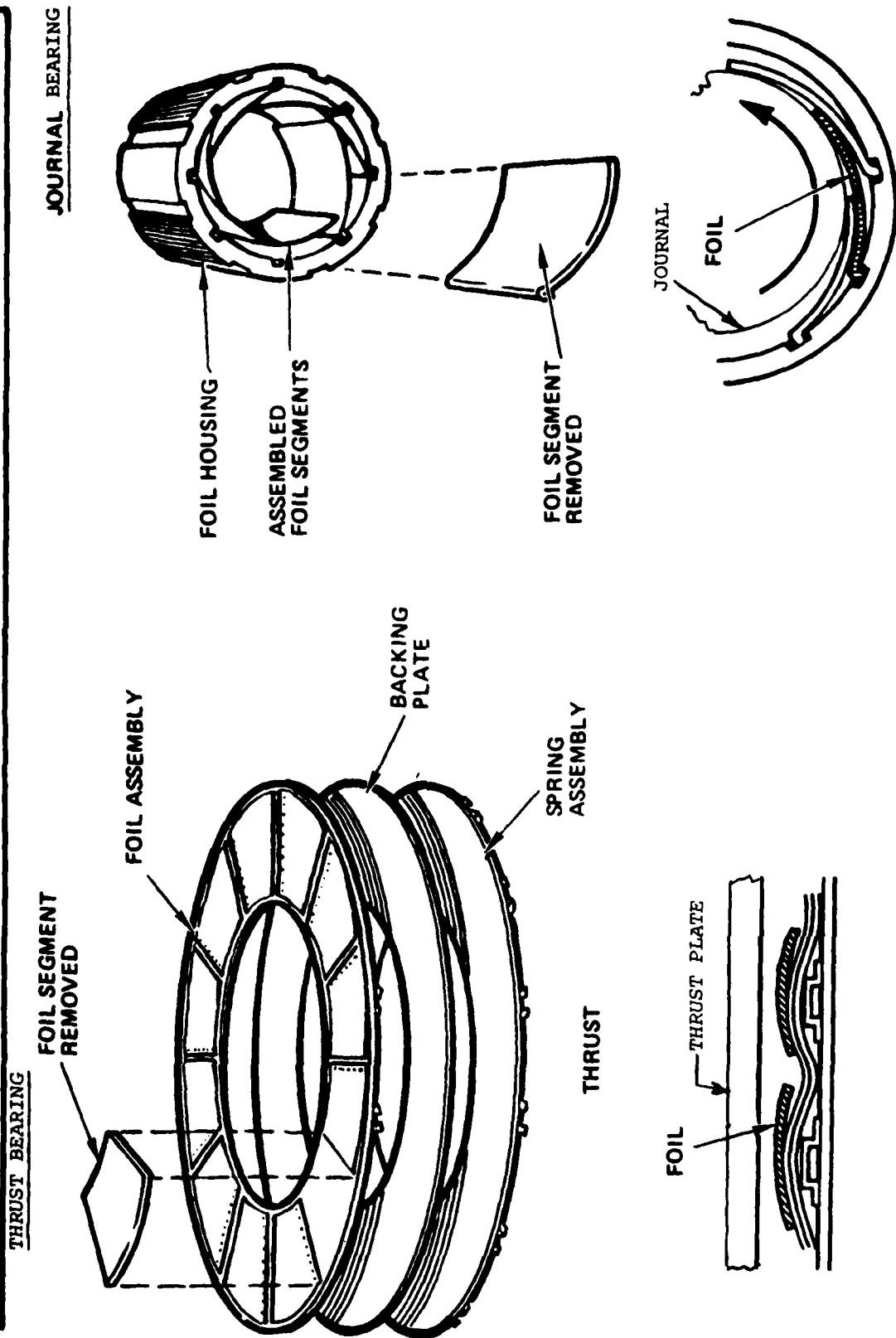


TABLE I: HIGH TEMPERATURE DEPOSITION TEST RESULTS
MONSANTO SKYLUBE 600 POLYPHENYL ETHER
BASED LUBRICANT

Test Conditions

Test Duration, hrs.	12	48	48	48
Oil-In Temp., °C (°F)	288 (550)	288 (550)	288 (550)	316 (600)
Max. Surface Temp. °C (°F)	427 (800)	399 (750)	427 (800)	454 (850)
Max. Oil Stream Temp. °C (°F)	338 (640)	329 (625)	338 (640)	366 (690)
Lower Deposition Tube Temp. °C (°F)	382 (720)	363 (685)	382 (720)	404 (760)
Environmental Temp. °C (°F)	204 (400)	204 (400)	204 (400)	204 (400)

Test Results

Total Deposits, mg	1	7	10	361
Tube Deposit Rating	0.5	6.0	9.8	381
Viscosity Change @ 38°C (100°F), %	8.0	14.7	17.4	51.1
TAN change	0.07	0.02	0.01	0.02
Consumption, ml	0	25	85	83
Filter Deposits, mg	0	70	63	869

TABLE II: HIGH TEMPERATURE DEPOSITION TEST RESULTS
EXPERIMENTAL POLYPHENYL ETHER
BASED LUBRICANT

Test Conditions

Test Duration, hrs.	48
Oil-In Temp., °C (°F)	302 (575)
Max. Surface Temp. °C (°F)	454 (850)
Max. Oil Stream Temp. °C (°F)	357 (675)
Lower Deposition Tube Temp. °C (°F)	399 (750)
Environmental Temp. °C (°F)	204 (400)

<u>Test Results</u>	<u>Basestock</u>	<u>NRL Inhibited Polyphenyl Ether</u>
Total Deposits, mg	107	13
Tube Deposit Rating	96	10.5
Viscosity Change @ 38°C (100°F), %	254	99.9
TAN change	0.28	0.34
Consumption, ml	65	60
Filter Deposits, mg	-	97

TABLE III: HIGH TEMPERATURE BEARING DEPOSITION

TEST RESULTS SKYLUBE 600
POLYPHENYL ETHER

<u>Test Conditions</u>	<u>MIL-L-23699C</u>	<u>Skylube 600 Test</u>
Oil-In Temp. °C (°F)	177 (350)	288 (550)
Oil Tank Temp. °C (°F)	199 (390)	310 (590)
Bearing Temp. °C (°F)	260 (500)	343 (650)
Duration, Hours	100	80

<u>Evaluation Characteristics</u>	<u>Specification Requirements</u>	<u>Test Results</u>
Deposit Demerit Rating	80 max.	107
Viscosity change @ 38°C (100°F), %	-5 to +30	230
TAN change	2 max.	-
Filter Deposits, g	3 max.	1.7
Oil Consumption, ml	2000 max.	2560

REFERENCES

1. AUTHORIZATION: NAVAIR AIRTASK A3303300/052B/4F54543300, Fuels and Lubricants, 10 August 1973 (Work Unit Plan 664).
2. TECHNICAL ARTICLE: Blenkiron, T. and Sawyer, W.J. Bristol Engine Div., Rolls Royce "Lubrication of the Olympus 593 Engine", Society of Automotive Engineers Air Transportation Meeting, 1968
3. REPORT: Mosier, S.A. and Johnson, M.L., Pratt and Whitney Aircraft, Florida Research and Development Center - "The Influence of Lubricants on Turbine Engine Design" Technical Report AFAPL-TR-70-9, April 1970.
4. CONTRACT: Exxon Research and Engineering Company "Investigation and Analysis of Advanced Hydrocarbon Fluids", U.S. Navy Contract No. N00019-70-C-0340, August 1970.
5. REPORT: Sumey, E.I., Russell, T.E., Hester, D.B., Methlie, J.E., General Electric Company, "Influence of Lubricants on Turbine Engine Design", Technical Report AFAPL-TR-70-54, September 1970
6. CONTRACT: Detroit Diesel Allison Division, GMC, "Advanced Attack Aircraft Engine", U.S. Navy Contract N00019-70-C-0588, November 1970
7. REPORT: Bucknell, R.L., Pratt and Whitney Aircraft Florida Research and Development Center, "Influence of Fuels and Lubricants on Turbine Engine Design and Performance", Technical Report AFAPL-TR-73-52, June 1973.
8. REPORT: Sumey, I.F., General Electric Company, "Fuels and Lubricants Influence on Turbine Engine Design and Performance", Technical Report AFAPL-TR-73-54, November 1974
9. TECHNICAL ARTICLE: Russell, T.E./Mattes, R.E., General Electric Co./McDonnell Aircraft Co., "A Study of High Temperature Fuels and Lubricants on Supersonic Aircraft/Engine System Performance", Society of Automotive Engineers, Air Transportation Meeting, 1974
10. TEXT: Guenderson, R.C. and Hart, A.W. "Synthetic Lubricants", Reinhold Publishing Co., New York 1962
11. TEXT: Braithwaite, E.R., "Lubrication and Lubricants", Elsevier Publishing Co., 1967
12. REPORT: Bowers, R.C. and Murphy, C.M., "Status of Research on Lubricants, Friction and Wear", Naval Research Laboratory, NRL Report 6466, January 19, 1967
13. REPORT: D'Orazio, A.J., Karpovich, P.A., Nowack, C.J., "A Study of the Factors Affecting Deposition Characteristics on Synthetic Lubricants for Gas Turbine Engines", Naval Air Propulsion Center, Report NAPC-PE-71, April 1974

14. REPORT: Waldron, W.D., Young, W.E., Curwen, P.W. Mechanical Technology Incorporated, "An Investigation of Air Bearings for Gas Turbine Engines", USAAMRDL Technical Report 71-59, December 1971
15. CONTRACT: AiResearch Manufacturing Company, "Evaluation of Gas Lubricated Hydrodynamic Bearings in a Gas Turbine Environment", U.S. Air Force Contract F33615-72-C-1376
16. SPECIFICATION: MIL-L-23699C, Lubricating Oil, Aircraft Turbine Engine, Synthetic Base, 4 October 1978
17. SPECIFICATION: PWA 524C, Lubricant, Aircraft Turbine Engine, Pratt and Whitney Aircraft, 6 June 1969
18. TECHNICAL ARTICLE: Ravner, H., Moniz, W.B., Blachly, C.H., Naval Research Laboratory, "High Temperature Stabilization of Polyphenyl Ethers by Inorganic Salts", American Society of Lubrication Engineers, ASLE 15,45 (1971).
19. TECHNICAL ARTICLE: Ravner, H., and Kaufman, S., Naval Research Laboratory, "High Temperature Stabilization of Polyphenyl Ethers by Soluble Metal-Organic Salts", American Society of Lubrication Engineers, ASLE 18,1 (1974)
20. TEST METHOD: Federal Test Method Standard No. 791B, Method 3410, "High Temperature Deposit and Oil Degradation Characteristics of Aviation Turbine Oils, 15 January 1969
21. PROJECT: NADC Work Request N62269/79/WR/00320 to NAPC, "Relationships Between Chemical Structures of Lubricants and Performance", 13 October 1978
22. CONTRACT: Mechanical Technology, Inc., "Pneumomechanical Critical Speed Control for Gas Turbine Engine Shafts", AF Contract F33615-72-C-1801
23. CONTRACT: AiResearch Manufacturing Co., "Pneumomechanical Critical Speed Control for Gas Turbine Engine Shafts", AF Contract F33615-72-C-2152
24. CONTRACT: AiResearch Manufacturing Co., "Dynamic and Environmental Evaluation of Compliant Foil Gas Lubricated Bearings", AF Contract F33615-72-C-1802
25. CONTRACT: Mechanical Technology, Inc., "Gas Lubricated Foil Bearing Technology Development for Propulsion and Power Systems", AF Contract F33615-72-C-1799
26. CONTRACT: AiResearch Manufacturing Co., "Gas Lubricated Foil Bearing Development for Advanced Turbo Machines", AF Contract F33615-73-C-2058

27. REPORT: Swenson, K.R., Hughes, N.M., Heuer, D.F., AiResearch Manufacturing Co., "Evaluation of Gas Lubricated Hydrodynamic Bearings in a Gas Turbine Environment". Technical Report AFAPL-TR-72-41 June 1972
28. REPORT: Waldron, W.D./Young, W.E., MTI/Pratt and Whitney Aircraft, "High Performance Bearing Study", Technical Report AFAPL-TR-72-63 July 1972
29. REPORT: Heuer, D.F., Collins, R.A., AiResearch Manufacturing Co., "Dynamic and Environmental Evaluation of Compliant Foil Gas Lubricated Bearings", Technical Report AFAPL-TR-73-56, June 1973
30. REPORT: Walowitz, J.A., et al, MTI, Inc., "Gas Lubricated Foil Bearing Technology Development for Propulsion and Power Systems", Technical Report AFAPL-TR-73-92, December 1973
31. REPORT: Rockett, T.J., et al, University of Rhode Island, "Performance Evaluation of Ceramic Materials and Aspects of Surface - Preparation for Gas-Bearings", Technical Report of 30 August 1975 for U.S. Navy Contract N00014-75C-0226
32. CONTRACT: AiResearch Manufacturing Co., "Gas Lubricated Foil Bearing Development for Advanced Turbomachines", U.S. Air Force contract F33615-73-C-2058
33. PURCHASE REQUEST: U.S. Air Force Aero Propulsion Laboratory, "Gas Lubricated Foil Bearings Development for Advanced Turbomachines", NAPC MIPR N62376-75-MP-00002, 7 January 1975
34. REPORT: Koepsel, W.F., AiResearch Manufacturing Co., "Gas Lubricated Foil Bearing Development for Advanced Turbomachines", Technical Report AFAPL-TR-114, Vol. I, March 1977
35. REPORT: Ravner, H., and Sniegowski, P.J., Naval Research Laboratory, "Additive Reactions in High Temperature Deposition Tests", NRL Memorandum Report 3644, November 1977

NRL Memorandum Report 3644

Additive Reactions in High Temperature Deposition Tests

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November 1977



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ADDITIVE REACTIONS IN HIGH TEMPERATURE DEPOSITION TESTS

INTRODUCTION

Navy aircraft gas turbine lubricants conforming to Specification MIL-L-23699 encounter operating temperatures ranging from minus 40°C at startup to 260°-290°C in the hottest engine areas. Bearing and main shaft temperatures may rise even higher due to heat soak-back after landing. One of the more serious problems arising from the heat burden on the lubricant is the formation of deposits on shafts and bearings, necessitating frequent overhauls and high maintenance costs. To help predict the deposit-formation tendencies of these oils, the Naval Air Propulsion Test Center (NAPTC), Trenton employs a device termed a "High Temperature Deposition Tester" (HTDT) in which oil is recycled in a prescribed routine past a gradient-heated tube; the type and quantity of deposits formed on the tube surface and the amount of solids retained on a line filter are all a measure of the stability of the oil with respect to the formation of solids (1).

In the course of an on-going joint NRL-NAPTC study of lubricant-additive chemical interactions at elevated temperatures in engine environments it became apparent that HTDT runs would not only provide deposition data, but could also yield qualitative chemical and kinetic data on the role and fate of the oxidation inhibitors as well. A program was therefore instituted in which NAPTC subjected a pentaerythritol ester-base, antioxidant-containing fluid of the type used in MIL-L-23699 formulations to runs in the HTDT rig under a variety of operating conditions; samples were periodically withdrawn for subsequent analysis at NRL. The present report summarizes the results to date of this study.

EXPERIMENTAL

The formulation employed in these experiments was a commercial pentaerythritol ester of primarily pentanoic acid containing varying proportions of the antioxidants phenyl-1-naphthylamine (PANA) and dioctyl diphenylamine (DODPA). Initially, the additives were analyzed by GLC using columns of 15 percent Dexsil-300 on Chromosorb W solid support. It was found, however, that after oxidation in the HTDT apparatus a degradation product of the ester was generated which overlapped the DODPA chromatographic peak and precluded analysis of the latter component; a wide variety of column packings were examined but they provided no improvement in the separation of the components. A

Note: Manuscript submitted October 27, 1977.

thin layer chromatographic (TLC) method was therefore developed which permitted analysis of the additives (2). Since the results using this procedure provided much of the basis for the study, an outline of the method is given here.

The equipment required for the TLC analysis included precoated 0.25 mm thick E. Merck Silica gel 60 F-254 10 x 20 cm plates, Centaur 100 microliter pipette with disposable plastic tips, Analtech 2-microliter disposable micro-pipettes, Chromato-Vue Model CC-20 viewing cabinet. Plates were precleaned by development in acetone and air dried one hour before use. The samples were diluted 3 to 1 with heptane and applied as duplicates in six 2-microliter spots along the 20 cm length of the plate 1.5 cm from the base. Standards containing 2, 1, 0.5, 0.3, 0.1, and 0.05 percent of each additive in the ester were prepared and spotted in duplicate on the plates. The spotted plates were developed in 50-50-heptane-toluene until the solvent front had risen 7.5 cm. Visualization of the additives on the air-dried plates was carried out in two ways:

1) Visualization in short wave UV light. The additive spots appeared as dark spots on the glowing green background of the plate. The 0.05 percent concentrations were just visible.

2) Examination in white light. After 24 hours the additive spots developed color and were conveniently viewed in white light. The 0.05 percent concentration was just visible. The R_f value (the ratio of the distance the component rises above the origin to the distance the solvent front rises) for DODPA is 0.76 and for PANA is 0.56. The base ester was not visible under the shortwave UV but could be detected in white light as a faint smudge with an R_f of about 0.1. Estimation of the additive concentrations was carried out by a visual comparison to the standards, with interpolation between values where necessary.

To provide information on deposit formation and additive depletion under simulated engine conditions, HTDT runs were usually programmed with oil-in temperature of 150°C and maximum tube temperature of 330°C, although other temperature limits were used on occasion. In the usual case, the test formulations were saturated during the runs with dry air to determine the effect of the presence of oxygen; however, in one series nitrogen was substituted for air.

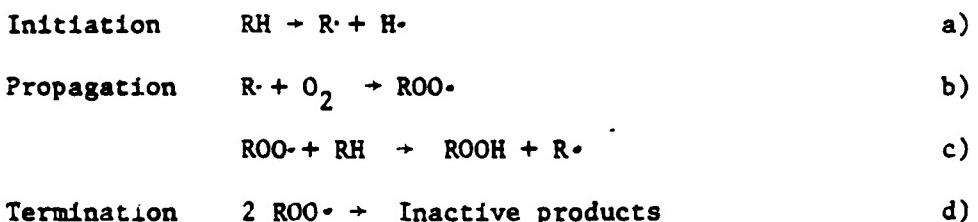
The initial lubricant charge in the HTDT apparatus was approximately 250 ml. Runs were generally continued until the viscosity increase of the oil approached 50 percent. There is some justification in referring to the 50 percent viscosity point as the induction period since a plot of viscosity vs time usually shows a sharp break in the curve in this region. In early runs, losses due to sample withdrawals, oil volatilization and degradation etc. were sufficiently large that make-up fluid was required to continue the runs. Such additions obviously

affected additive levels and possibly influenced the additive-lubricant reactions because of the antioxidant replenishment; in any event, they made analytic treatment of the data highly uncertain. A series of runs was therefore conducted without the addition of make-up oil. The oil-in temperature was 150°C and the maximum tube temperature was 330°C. The experiments were terminated either at the end of the induction period, i.e., oil viscosity increased by 50 percent, or when fluid levels were so low, ca. 150 ml, that the system could not operate. Except where indicated this report will deal with the results of these latter series of experiments.

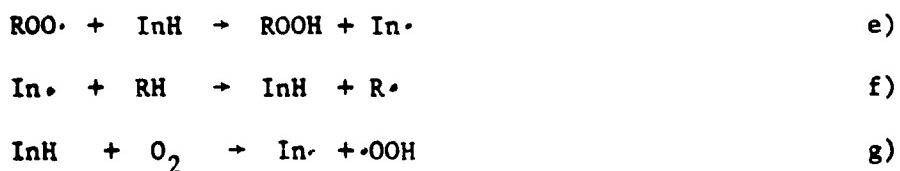
Analyses for additive contents were performed at NRL; viscosity and tube deposit measurements were made at NAPTC. The original NAPTC formulation used in each HTDT run is designated in the Tables by a PE-5L prefix; the runs themselves are identified by their NAPTC test numbers. In some instances, repeat runs with different test numbers were conducted to obtain different types of information, e.g., induction time, additive analysis, deposits, etc.

RESULTS AND DISCUSSION

Table 1 summarizes the results of the analyses for additive contents. With few exceptions, which are discussed in a later section, their concentrations decreased to only nominal amounts when the end of the induction period was reached. Before we discuss the factors affecting the kinetics of the additive depletion processes, it will be useful to review briefly the general mechanisms leading to the oxidation of the ester lubricant and the reactions of the additives. The air oxidation of hydrocarbons, esters, and many related organic compounds proceeds by an autocatalytic chain reaction:



The overall reactions in an inhibited system can be generalized as follows:



Equation (c) represents the early stage of the autoxidation of the oil; it involves the abstraction of a hydrogen atom from a molecule of the oil by a peroxy radical to form a hydroperoxide, and an active free radical R· which in turn quickly reacts with oxygen in the air to form another peroxy radical. In equation (e) preferential reaction of the peroxy radical with an inhibitor tends to quench the reaction, provided the In· radical is relatively inactive. Therefore, for effective inhibition reaction (f) should be very slow compared to reaction (c). It is also expected that some of the inhibitor, especially at elevated temperatures, will also react directly with atmospheric oxygen, reaction (g). The significance of these reactions is to demonstrate that the inhibitor can be depleted by two routes, one by the reaction with peroxy radicals and the other by reaction with atmospheric oxygen. Obviously there are various secondary reactions here that could further complicate the situation; these will not be considered here.

Under operating conditions in the High Temperature Deposition Tester, it is assumed that ROO· radicals are generated at a constant rate, corresponding to a zero order reaction which does not depend upon the amount of additive present. Rate of depletion of the inhibitor by oxygen, on the other hand, depends upon the concentration of the additive and the concentration of oxygen. Since air is continuously passed through the oil, the concentration of oxygen is held constant and the reaction is therefore first order. The rate of additive depletion is thus postulated as:

$$\frac{-dC}{dt} = k_o + k_1 C$$

where C is the concentration of the inhibitor. Integration of this expression between C_0 , the original concentration and C , the final concentration after t time leads to:

$$t = -\ln \left[\frac{k_o + k_1 C}{k_o + C_0 k_1} \right] / k_1 . \quad (\text{Equation 1})$$

When t is the induction period, C is essentially zero so that the term $k_1 C$ drops out:

$$\text{induction time} = -\ln \left[\frac{k_o}{k_o + C_0 k_1} \right] / k_1 \quad (\text{Equation 2})$$

Concentration terms are in percent and time is in hours. Since the time for the oil without inhibitor to reach a 50 percent viscosity increase was six hours, this "blank" time was subtracted from the experimental values in the subsequent calculations. From the data in Table 2 best values were determined for the rate constants by substitution into equation 1. For PANA, $k_o = 0.0027$ percent hr⁻¹ and $k_1 = 0.020$ hr⁻¹; for

DODPA, $k_0 = 0.020$ percent hr⁻¹ and $k_1 = 0.010$ hr⁻¹. The k_0 value for DODPA is six times that of PANA when expressed in the above units. When concentrations are expressed in moles per liter the k_0 constant for DODPA is only three times as great. The two curves in Figure 1 were constructed from these values of k_0 and k_1 , substituted into Equation 2. Although only a small quantity of data were available, this somewhat simplified kinetic model reasonably fits the results.

If we consider a system in which there are two additives present that inhibit independently while both are undergoing oxidation, equation 2 can be used to predict the resulting induction time. Assume that either PANA or DODPA inhibits the system until the additive is completely depleted; time t for depletion to occur is calculated from equation 2. At the end of this time, the concentration of the other additive changes from C_0 to $(C_0 e^{-k_1 t})$ because of its oxidation in air; now the induction time of this additive at the new concentration can also be calculated. Similar calculations are also made based upon the assumption that the other additive reacts first. Predicted induction times can thus be given as a range of two values. In Table 3 the first value of the predicted range for the additive mixtures was determined as if DODPA inhibited initially. In each such case the expected range for the induction period is greater than that actually found. Application of Student's t-test in the 0.05 probability range shows a significant difference between experimental values and the mid-values of the predicted ranges. Thus some type of interaction between the two additives is suggested. Confirmation of this by TLC results is given in a later section.

The HTDT and analytical data indicate that in formulations containing mixtures of the two additives, PANA is depleted faster than DODPA, e.g. in Test Nos. 531 and 547 the ratio of DODPA to PANA became progressively larger as the testing proceeded. Such a trend is not entirely unexpected, and the ratio of the induction times of two additives of equal starting concentrations is commonly used as a rough way of evaluating the relative reaction rates of the inhibitors with the peroxy radicals. The inhibitor which reacts faster with these radicals will have the longer induction time since it is more effective in quenching the chain reaction and thus limits the generation of additional radicals. If the two additives were used together it would thus be reasonable to expect that the more effective additive would be preferentially consumed since it would react with more free radicals than the less efficient one.

Thin layer chromatograms of samples taken during the testing periods revealed components other than the two original additives. Components that fluoresce brilliantly under long wave UV light were readily seen in freshly developed TLC plates. After several hours the fluorescence diminished and was replaced by colors visible in white light. In systems that reached the end of the induction period, TLC revealed only brownish-orange materials that remained at the origin of

spotting. Although no attempt has yet been made to clarify these observations, it is speculated that the brightly colored components are derivatives of the additives as they are progressively oxidized. Chromatograms of samples of mixtures of the additives showed, during the early periods of testing, several components that did not form when the additives are used separately in the base oil. As mentioned earlier, this suggests interaction of the two additives.

The loss of the additives by oxidative degradation during the HTDT runs was confirmed in a different series of experiments. Formulation PE 5L-685, containing 1.0 percent each of PANA and DODPA, was subjected to four HTDT runs in which oil-in and maximum surface temperatures ranged from 149°C to 204°C, and 330°C to 399°C respectively, Table 4. The calculated organic nitrogen content of this formulation due to the additives was 0.13 weight percent; the analyzed content (by a commercial laboratory) was 0.10 percent. In these runs, varying amounts of make-up PE 5L-685 were added as required. As seen in Table 4, in the course of these runs analyzed nitrogen contents remained essentially unchanged, even though the original additives had in some cases been completely depleted. (That the nitrogen content did not increase due to makeup oil additions is probably a result of venting losses and sampling withdrawals.) It is reasonable to assume that the residual nitrogen represents oxidized additive content, particularly when taken in conjunction with the TLC results.

The presence or absence of HTDT tube deposits is of overriding significance from an operational point of view. It is obvious from the results in Table 5 that under aeration conditions, the base stock ester does not generate deposits. PANA, however, in concentrations above ca. 0.2 percent, was a major cause of deposit formation; DODPA, on the other hand, had essentially no such effect. When PANA and DODPA were simultaneously present, DODPA did not inhibit the PANA-induced deposits. From the data in Table 5 where aeration conditions were used, a plot of the original percent PANA vs. the milligrams of deposit was constructed, as shown in Figure 2. The regression line calculated by the least squares method gives:

$$\text{Mg tube deposits} = (470) (\% \text{ PANA}) - 70$$

When the HTDT tests were conducted in an atmosphere of nitrogen, Table 5, no deposits were generated, even under very high oil-inlet and outlet temperatures. Although the scope of the present study did not include the chemistry of deposit formation, the interaction of PANA with oxygen to produce these deposits and the inertness of DODPA in this respect are of great practical interest and significance, and their causes should be pursued.

SUMMARY AND CONCLUSIONS

The preliminary phase of a joint NRL/NAPTC study of additive depletion in an ester-based formulation was concluded using the HTDT rig as a test system. An expression relating induction times and original concentrations of PANA and DODPA inhibitors was devised based on simple kinetics of an inhibited system. Predictions were generally satisfactory where the inhibitors were used singly but less so with mixtures of the two additives; interaction of the two additives is suspected. PANA was shown to be a more effective inhibitor than DODPA; it was also a more serious deposit generator under aeration, but not under a nitrogen blanket. From the data reported here, little advantage was seen in the use of mixtures of the two additives either in extending the induction period or in reducing deposits under conditions in the HTDT rig.

FUTURE WORK

Based on the results of this preliminary study, a follow-on effort will be continued as indicated:

1. Individual oxidation products of both PANA and DODPA will be generated and identified to provide clues as to the separate roles they play in the ester-inhibition process. This may be conveniently carried out in controlled laboratory tests using the gas chromatograph-mass spectrographic system now available in the Tribology Section.
2. A laboratory study will be made of PANA and DODPA (or other model additive systems) to examine their interactions in an ester base under oxidizing conditions.
3. It would be advantageous if the continuing research effort with NAPTC would include small engine testing of model formulations. A realistic comparison could then be made with "real life" oil-additive behavior and these kinetic model studies.

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REFERENCES

1. "A Study of the Factors Affecting Deposition Characteristics of Synthetic Lubricants for Gas Turbine Engines", D'Orazio, A. J., Karpovich, P. A., and Nowack, C. J., Naval Air Propulsion Test Center, Trenton, N. J. report NAPTC-PE-71, April 1976.
2. "Quantitative TLC Analysis of Amine Antioxidants in High-Temperature Jet Engine Lubricants", Paul J. Sniegowski, NRL Memo Report 3490, April 1977; also published in the Journal of Chromatographic Science 15, August 1977, p. 328.

Table 1
HTDT Analytical Data
Oil-In 149°C, Maximum Surface Temperature 330°C

<u>Run</u>	<u>Test Hrs.</u>	<u>Z Additive</u>	<u>PANA</u>	<u>DODPA</u>	<u>Viscosity Increase</u>
1A - No Additive Present					
PE-5L-682 Test 458-1	10	0 0	0 0	0 0	95
1B - PANA Present					
PE-5L-765 Test 535-1 -2	5 50	0.2 0.05 (b)	0 0 0	0 0 0	0.9 50
PE-5L-766 Test 541-1	84	1.0 (a)	0 (a)	0 (a)	50
PE-5L-767 Test 545-1 -2 -3	25 50 76	2.0 1.5 0.1 (b)	0 0 0 0	0 0 0 0	4.9 11 14
1C - DODPA Present					
PE-5L-768 Test 540-1 -2 -3	8 10 12	0 0 0	0.2 (b) (b)	0 (b) (b)	21 45 96
PE-5L-769 Test 638-1	50	0 0	0 (a)	1.0 (a)	25
PE-5L-770 Test 673	79	0 0	0 (b)	2.0 (b)	63
1D - PANA and DODPA Present					
PE-5L-738 Test 488-1	36	0.2 (a)	0.2 (a)	0.2 (a)	50
PE-5L-749 Test 519-1 -3 -4	25 37 54	0.2 (b) (b) (b)	1.0 0.4 0.1 (b)	1.0 0.4 0.1 (b)	6.2 7.8 62
PE-5L-771 Test 548-1 -3 -4	25 37 54	0.2 (b) (b) (b)	2.0 0.6 0.07 (b)	2.0 0.6 0.07 (b)	7.0 23 54
PE-5L-683 Test 547-1 -2 -3	25 50 75	1.0 0.2 0.1 0.05	1.0 0.5 0.3 0.2	1.0 0.5 0.3 0.2	20 31 66
PE-5L-746 Test 531-1 -3 -5	25 65 80	2.0 0.2 (b) (b)	1.0 0.5 0.1 0.05	1.0 0.5 0.1 0.05	8.2 37

(a) No analyses performed for additive content.

(b) Additive content below detectable limit of 0.05 percent.

Table 2

**Effect of Individual Additive Concentration
on Induction Times**

<u>Test No.</u>	<u>Orig. %</u>	<u>PANA</u>	<u>DODPA</u>	<u>Induction Time</u> <u>(Corrected)</u>
545	2.0	0		134
541	1.0	0		84
535	0.2	0		44
540	0	0.2		7
678	0	1.0		49
673	0	2.0		71

Table 3

Effect of Mixed Additives on Induction Times

<u>Test No.</u>	<u>Orig. %</u>	<u>PANA</u>	<u>DODPA</u>	<u>Induction Time</u> <u>(Corrected)</u>	<u>Calculated Range of</u> <u>Induction Time</u>
488	0.2	0.2		30	43 - 45
531	2.0	1.0		79	132 - 140
548	0.2	2.0		79	82 - 91
547	1.0	1.0		63	104 - 137
519	0.2	1.0		49	62 - 68

Table 4
Organic Nitrogen Contents of HTDT-Subjected Oil

<u>Sample</u>	<u>Test Hours</u>	<u>PANA</u>	<u>DODPA</u>	<u>% Nitrogen Found</u>
PE3L-685		1.0	1.0	0.10 ^(a)
		Oil-In 149°C	Maximum Surface Temp. 330°C	
431	25	0.1	0.5	(b)
	50	0.1	0.5	.09
	75	0.05	0.3	.09
	110	0.1	0.1	.09
		Oil-In 149°C	Maximum Surface Temp. 343°C	
425	50	(c)	0.2	(b)
	100	(c)	0.1	(b)
	110	(c)	0.05	0.12
		Oil-In 204°C	Maximum Surface Temp. 385°C	
430	7	(c)	0.1	0.08
	10	(c)	(c)	
	12	(c)	(c)	0.10
		Oil-In 204°C	Maximum Surface Temp. 399°C	
429	3	0.2	0.3	(b)
	4.5	(c)	(c)	(b)
	6	(c)	0.1	(b)
	7	(c)	(c)	0.10

- (a) Calculated organic nitrogen content based on original additive content is 0.13 weight percent.
- (b) No analyses performed for additive content.
- (c) Additive content below detectable limit of 0.05 percent.

Table 5

Tube Deposits

Air Atmosphere
Oil-In 149°C Maximum Surface Temp. 330°C

<u>Test No.</u>	<u>Tube Deposits, mg.</u>	<u>Original %</u>	
		<u>PANA</u>	<u>DODPA</u>
458	2	0	0
545	978	2.0	0
531	712	2.0	1.0
547	480	1.0	1.0
541	419	1.0	0
535	13	0.2	0
540	8	0	0.2
673	0	0	2.0
519	3	0.2	1.0
548	2	0.2	2.0

Nitrogen Gas Atmosphere
Oil-In 149°C Maximum Surface Temp. 330°C

473	1	1.0	1.0
Oil-In 204°C Maximum Surface Temp. 413°C			
474	1	1.0	1.0

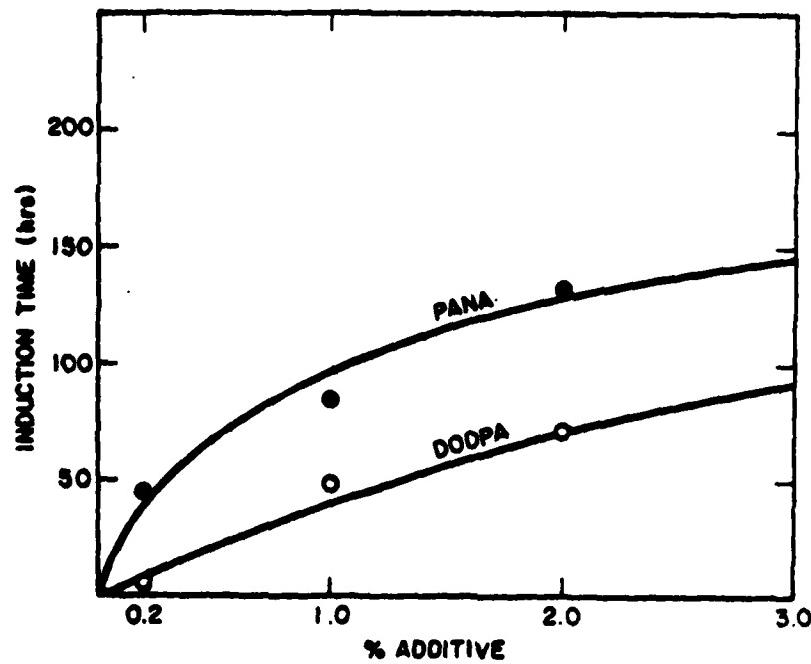


Fig. 1 — Induction time as a function of additive content

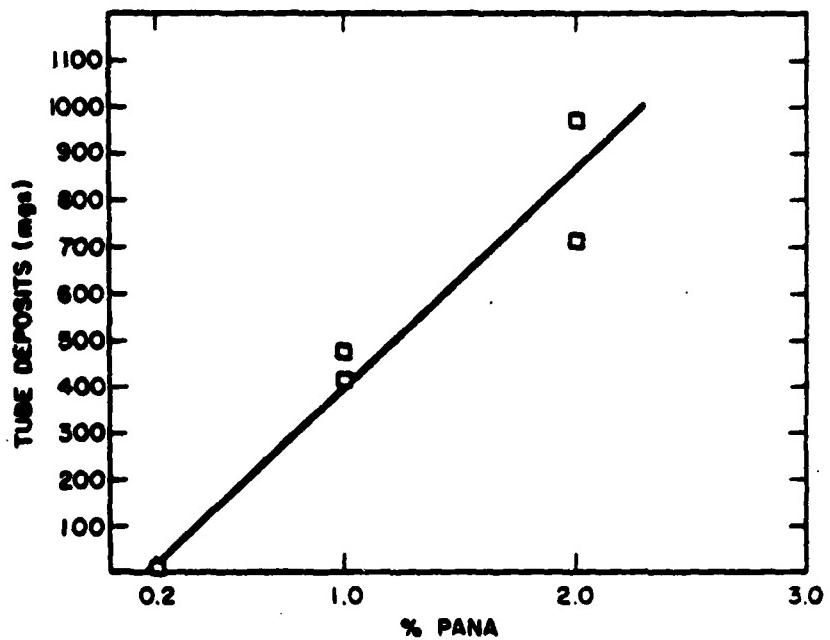


Fig. 2 — Tube deposits as a function of PANA content